Molecular Dynamics and Morphology of Polyether–Polyurethane Elastomers under Extension by ^{13}C MAS-NMR

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Received May 24, 1991; Revised Manuscript Received October 19, 1991

ABSTRACT: The ^{13}C NMR spectra and relaxation times of Lycra 146, a segmented copolymer of a poly(tetramethylene glycol) (polyTMG) chain extended with 4,4′-methylenebis(phenyl isocyanate) (MDI) and MDI linked with ethylene glycol were examined as a function of extension. A novel method of spooling the long yarns and spinning them at 5 kHz in a magic angle spinning NMR probe allowed examination of both "soft" and "hard" segment mobilities and estimation of respective fractions of domains. The characteristic times for cross polarization (T_{CH}), rotating-frame relaxation ($T_{1\rho}{}^{H}$), and dipolar dephasing ($T_2{}^*$) were sensitive to even moderate extension. $T_1{}^{H}$ and $T_1{}^{C}$ changed only at extreme extension, with the latter exhibiting multicomponent decay. The results are interpreted in terms of crystalline and amorphous domain sizes and the relative amounts of each. The fraction of rigid MDI was found to be lower than the fraction of MDI in the hard segments, indicating incomplete phase separation or at least significant interpenetration of phases.

Polyurethane thermoplastic elastomers (TPE) possess an excellent range of properties and are the material of choice for many applications. These segmented block copolymers are characterized by "hard" and "soft" domains as shown by many techniques. Segmented block copolymers have been investigated by solid-state NMR by others,[6,7] and there is a vast literature on the study of semicrystalline systems[8] with the early and continuing detailed work done by VanderHart.[9] The soft segments can be either polyether or polyester, and the hard segments can be either urethanes or ureas. In the previous paper[10] we reported the study of phase structure by ^{13}C MAS-NMR on polyester–polyurethane elastomers for both relaxed and extended states. The effects of elongation on the two domains have been observed. In this paper we describe a similar study on a polyether–polyurethane elastomer and have obtained results on domain sizes, relative amounts of each domain, and the effect of strain on them.

Experimental Section

Lycra 146 is a product of E. I. du Pont de Nemours and Co. It is manufactured by chain extension of poly(tetramethylene glycol) (polyTMG) of molecular weight 2000 with excess 4,4′-methylenebis(phenyl isocyanate) (MDI) and coupled with low molecular weight diol or diamine. On the basis of the 45 ppm line in the solid-state NMR spectra, ethylene glycol (EG) is probably the coupling diol. The urethane components constitute the hard segments which amounted to 15 wt % of the polymer; the chain-extended polyTMG acts as the soft segment. The sample was received as 420 denier (1 denier = 1 g/9000 m) of yarn. It was wound onto Delrin or Kel-F spools under a constant tension and slip fit into the 6-mm-i.d. ceramic Doty rotor.[10] A few early samples were made by simply winding the yarn around a 1.5-mm wooden dowel at the desired extension. These were not spun and are designated as "nonspinning" in the relevant data sets.

^{13}C NMR spectra were obtained at 50.3 MHz with a 200 AF IBM NMR spectrometer with an IBM Solids Accessory and Doty Scientific (Columbia, SC) CP-MAS probe. Carbon and proton powers were set for 5-μs 90° pulses. Spectra were generally obtained with spinning at or near 5 kHz and with 50 kHz decoupling power. Pulse sequences for cross polarization (CP), direct polarization (DP = simple Bloch decay), proton spin–lattice relaxation time ($T_1{}^{H}$), proton spin–lattice relaxation time in the rotating frame ($T_{1\rho}{}^{H}$), carbon spin–lattice relaxation time ($T_1{}^{C}$), carbon–proton cross-polarization time (T_{CH}), transverse relaxation time ($T_2{}^*$), and the fitting routines for multiple time constants were all described in a previous paper.[10]

Results and Discussion

As a preface to the results we point out that while it is sometimes helpful to think of these systems in terms of hard and soft segments, they are obviously more heterogeneous with a variety of possible morphologies and corresponding mobilities—crystalline, glassy, rubbery, and amorphous domains are possible for each "phase" as well as the several possibilities of interpenetration or mixing of the urethane and polyTMG segments. Systems very similar to these have been studied[5] by DSC and X-ray techniques, demonstrating clearly that polyTMG crystallinity is present and increases with extension. PolyTMG has a melting point at about 35–40 °C depending on molecular weight, so it is not surprising that the lowering entropy with extension induces some crystallinity. Its glass transition is at −84 °C, so there is no possibility of ordinary glassy mobility of polyTMG segments for the experiments reported here which were all done at 20 °C. The MDI–ethylene glycol hard segments are well-known to have much higher glass and melting transitions of 173 and 239 °C, so both morphologies may be present under our experimental conditions. There is no available high-temperature DSC data for these samples to help positively distinguish glassy from crystalline components. However, it must be appreciated that "hydrogen-bridged para-crystallinity" of the hard segments was found in the original wide-angle X-ray crystallographic study by Bonart[2] of polyurethanes–polyethers similar to those of this study. Bimodal relaxation and deuterium NMR line shapes, assigned respectively to crystalline and amorphous domains, have been found in similar MDI-polyTMG hard segments.[6]

Spectral Observations. Figure 1A shows the ^{13}C NMR DP spectrum obtained following a 90° pulse with decoupling for a nonspinning sample of Lycra 146 with a 3-s recycle time. The prominent features of the weak spectrum are the 26 and 70 ppm resonances which are respectively the CH_2 and OCH_2 carbons of the polyTMG segments in the elastomer. These resonances are about 400 Hz wide which is an index of high mobility in the "solid" state. Also evident is a 1500-Hz-wide, weak, featureless peak in the aromatic region of 110-140 ppm which arises from the aromatic carbons of MDI. This line arises from a number of inequivalent aromatic carbons which have chemical shift anisotropies on the order of 10 kHz so that at least some of the hard segments are mo-

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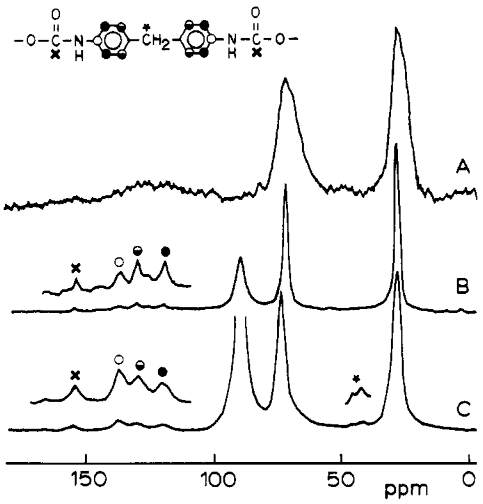

Figure 1. ^{13}C NMR spectrum at 50 MHz of Lycra 146: (A) nonspinning sample, Bloch decay with a 3-s recycle time; (B) unstretched sample spinning at 5 kHz, Bloch decay with a 3-s recycle time. The inset shows part of a MDI moiety with designated assignments of peaks in the aromatic region (the peak at 90 ppm arises from the Delrin spool); (C) stretched sample of $\lambda = 5$, CP-MAS.

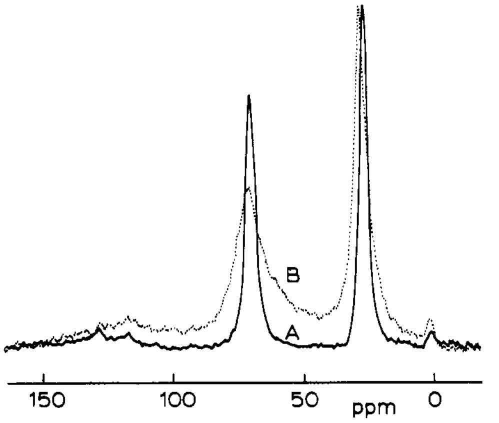

Figure 2. Line shapes of nonspinning Lycra 146 samples as a function of the extension ratio: (A) $\lambda = 1$, (B) $\lambda = 6.2$.

tionally narrowed and not all the hard segments are immobile.

Magic angle spinning with strong proton decoupling narrowed the CH_2 carbon lines of an unstretched sample to less than 100 Hz. Some aromatic peaks also emerged as seen in Figure 1B. The better resolved peaks at 118, 128, 136, and 154 ppm correspond closely to typical chemical shifts of carbons as assigned in the inset to the figure. The observability of these peaks by DP with a short recycle time requires a short T_1^C in contrast to the long carbon T_1^C described below for the "rigid" phase. This indicates that these aromatic peaks in the unstretched sample arise from those MDI which are not in crystalline or glassy domains and surely include the MDI employed to chain extend the polyTMG segments.

The effect of stretching the sample is evident in the CP spectrum (Figure 1C). Compared to the spectrum in Figure 1B of an unstretched specimen, the CH_2 peaks are broader by almost a factor of 2 and the aromatic peaks shift in intensity. A pair of weak peaks at 45 and 41 ppm appear which we assign respectively to the CH_2O of EG and the CH_2 of MDI.[11]

Stretching a nonspinning sample has a dramatic effect on the line shape as shown in Figure 2: the aliphatic peaks become broader with extension, and the CH_2 resonance shows a 1 ppm downfield shift in the $\lambda = 6.2$ sample.

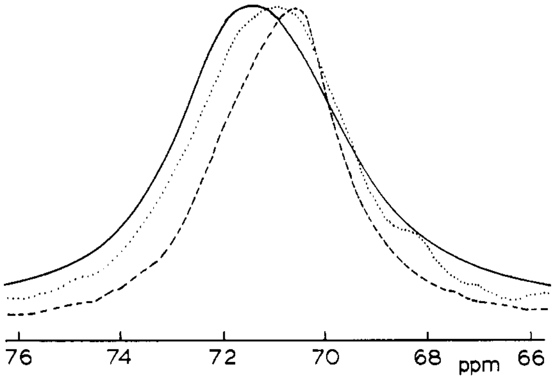

Figure 3. Comparison of expanded ^{13}C MAS-NMR spectra of the 70 ppm region for Lycra 146 extended 5-fold, obtained by various pulse sequences. All spectra are normalized to the same height and do not demonstrate any relative intensity relationship but only peak positions: (A) (- - -) Bloch decay with a 3-s recycle time (19 028 scans); (B) (···) Bloch decay with a 600-s recycle time (144 scans); (C) (—) cross polarization, 2-ms CP time (6051 scans).

The spectral resolution can in general be improved by MAS, but each spectral line has contributions from different domains and we must rely on relaxation for "resolution". However, the disparity in relaxation times of segments belonging to different domains (vide infra) means that, in order to observe all domains with equal sensitivity, long recycle delays of up to 300 s for Bloch decays are necessary. The spectrum of Figure 1C was obtained by cross polarization and thus may emphasize those carbons more tightly coupled to protons. The selectivity is demonstrated by the peak positions in the expansions of the 70 ppm region in Figure 3 for several pulse sequences.

The OCH_2 resonance at 72 ppm was not detected by DP with a recycle time of 3 s, which is much shorter than T_1^C. The resonance of the most mobile carbons is near 70 ppm, which requires a large number of transients. In order to include resonances of all carbons at full intensity the recycle time must be at least 5 times T_1. It can be seen from the spectrum in Figure 3b that using a 600-s recycle time for Bloch decay gives a composite resonance with an apparent position between the two at 70.9 ppm. Given the narrowness of the 70 ppm peak and the shape of the composite resonance, it is clear that there is a third component present, as is detailed below.

The assignment of contributions to the 70 ppm region can also be clarified by examining the spectra of polyTMG itself. This has recently been studied by ^{13}C NMR in excellent detail by Hirai et al.,[12] who were able to cleanly discern separate relaxations and spectral contributions of crystalline, amorphous, and interfacial segments to the "70 ppm" line. In Figure 4 are shown our spectra of 2000 MW polyTMG obtained under the same variety of pulse sequences as that for extended Lycra 146. Figure 4A is for Bloch decay with a 3-s recycle time, thus displaying only the amorphous or freely moving segments. Figure 4B shows the result for cross polarization which clearly favors the rigid polyTMG crystalline phase but does observe the amorphous species albeit weakly. Figure 4C is for long recycle time Bloch decay giving equal weighting to all carbons present. There is a distinct shoulder at 72 ppm and a strong amorphous peak at 70 ppm. Figure 4D is the DP spectrum of Lycra 146 at full extension for a long recycle time. This shows there is no observable "amorphous" polyTMG phase in this specimen. Given that there is "crystalline" phase, the observed resonance of Figure 4D is clearly a composite of the crystalline peak

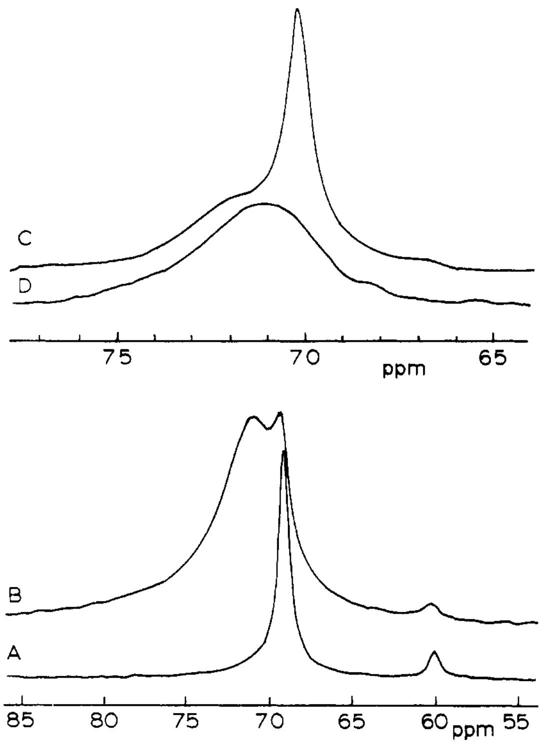

Figure 4. ^{13}C MAS-NMR spectra of polyTMG (MW 2000): (A) Bloch decay, 3-s recycle time; (B) cross polarization, 2-ms CP time; (C) Bloch decay, 600-s recycle time, 45° pulse; (D) Lycra 146 sample at high extension ($\lambda = 5$) for comparison, Bloch decay, 600-s recycle time.

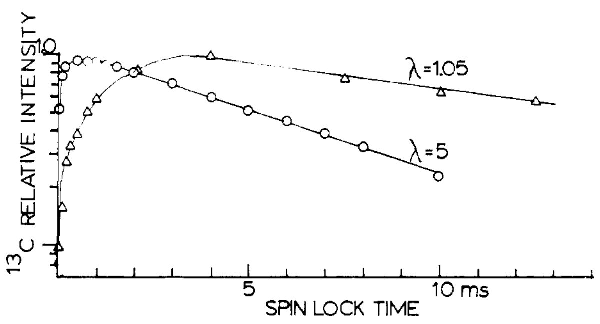

Figure 5. Cross-polarization dynamics and $T_{1\rho}^{H}$ decay for CH_2 segments (26.4 ppm) of Lycra 146 extended 10.5 times (△) and 5 times (○) for a 50-kHz proton and carbon radio-frequency field at 20 °C.

and a third component. Lorentzian curve resolution gives peaks at 72 and 70.8 ppm in an area ratio of 65:35. This is in very satisfactory agreement with the relaxation data below. These small chemical shifts caused by elongation are a result of the well-known effects of changing the relative populations of gauche and trans conformers contributing to the average chemical shift.[13] This third component at 70.8 ppm must be polyTMG segments of intermediate average conformation, i.e., between the crystalline gauche conformation (polyTMG is helical) and whatever the trans/gauche average conformation is in amorphous polyTMG. This intermediate value can only arise from distortion of chains.

Relaxation Observations. The dynamics of cross polarization of CH_2 segments (26.4 ppm) show dramatic differences between stretched and unstretched Lycra 146 as shown in Figure 5. The unstretched sample shows what is clearly a multiphasic growth of intensity which does not reach a maximum until about 3 ms and then decays slowly. The stretched sample reaches its maximum intensity in less than 1 ms and decays much more rapidly. These data were fit to an equation for the increases in magnetization of two different species;[14] the results are presented in Table I.

Table I
Relaxation Parameters for Lycra 146 Related to Cross-Polarization Dynamics

		CH_2:	OCH_2:	aromatic C	
	λ	26.4 ppm	70.5 ppm	127 ppm	136 ppm
T_{CH},[a] ms	1	2.7 (92%)	2.0 (93%)	0.60 (70%)	1.52 (75%)
		0.05 (8%)	0.02 (8%)	0.03 (30%)	0.1 (25%)
	5	1.3 (29%)	0.60 (23%)	0.19 (18%)	0.55 (44%)
		0.07 (71%)	0.05 (77%)	0.06 (82%)	0.10 (56%)
$T_{1\rho}^{H}$,[b] ms	1	27.2	12.1	6.4	7.1
MAS	5	6.2	6.9	5.9	5.9
$T_{1\rho}^{H}$,[c] ms	1	25	16		
non-MAS	3	12	10		
	4.5	11	5.3		
	6.2	8.9	4.0		

[a,b] Fit to two separate domains with discrete T_{CH}'s but the same $T_{1\rho}^{H}$. [c] Samples were wound around a 1.5-mm wooden dowel; $T_{1\rho}^{H}$ was measured from the logarithmic decay of the ^{13}C intensity. There appeared to be a long $T_{1\rho}^{H}$ base in the decay presumably from material on the edge of the effective spin-lock field. These are initial slope values.

The range of T_{CH} values for protonated carbons in Table I covers almost 2 orders of magnitude, indicating a strong sensitivity to the motional environment of the segments. The longest value is 2.7 ms in the unstretched polyTMG segments of Lycra 146. This value is very close to that found for other mobile CH_2 groups above T_g.[15] However, a small fraction of the segments have a dramatically shorter T_{CH} value of 0.05 ms which must be from the rigid portion of the polyTMG even in this unstretched sample. Assignment of these components to crystalline domains is based on the DSC and X-ray results of ref 5. Extension of the sample by 5-fold strongly shifts the relative quantities of rigid and bulklike free segments but does not substantially change the T_{CH} values for each domain. The CH_2O segments behave similarly but with a somewhat larger change of T_{CH} values for the bulk material. In the polyester–polyurethane[10] Lycra 128, there were observed three distinct ranges of T_{CH} which were assigned to bulk, strained, and crystalline phases. The polyester is more reluctant to crystallize, and so there would be a larger component of strained, noncrystalline segments than in the easily crystallized polyTMG segments.

The aromatic resonances from the polyurethane sequences of the polymer show a very distinct heterogeneity in the cross-polarization dynamics (T_{CH}) for both the stretched and unstretched sample (Table I). The T_{CH} values of the two components differ by more than an order of magnitude, and the relative contributions of each component change dramatically with extension. Bearing in mind the above caveat about the high glass and melting transitions for these segments, these two relaxation components may be assigned among three candidates: crystalline, glass, and isolated aromatic segments. These last listed segments have been seen by infrared studies[16] and are expected simply from the chemical synthesis which places 42%[17] of the MDI as chain extender in the polyTMG segments. On the basis of the T_{CH} data of Table I and assuming equal efficiency of cross polarization of protonated aromatic groups of each morphology, it appears that 70% of the hard segments, i.e., an excess over the expected, are moving relatively freely in the unstretched material. In the stretched material under the same assumptions a larger portion than expected of the aromatic segments are rigid so that some of the chain-extending segments, freely moving in the unstretched material, are in rigid environments in the stretched material. The assumption of equal efficiency for all carbons contributing to the protonated aromatic resonance at 127 ppm is not a farfetched one. Cross polarization will be dominated by the bonded proton, and the times for all these polarization transfers are short, indicating high efficiency. For the unprotonated aromatic resonances at 136 ppm the efficiency depends on the more distant protons of the environment which will vary with morphology and thus would be more questionable than the data for the protonated resonance. As mentioned above it is not possible to decide via NMR alone whether the more rigid component is glassy or crystalline, but because the isolated hard segments have been seen by other techniques it seems clear that the more freely moving segments can be assigned to that population of segments in the soft domains. These observations also agree with the initial observation of Figure 1A that some of the aromatic groups were relatively free to move, giving rise to a broad peak in the nonspinning sample.

The dependence of $T_{1\rho}{}^{H}$ on extension (Table I) is marked. It is well understood that $T_{1\rho}$ may have two major contributions, one motional and one direct dipolar. The latter can become more pronounced with crystallization. Thus it is not feasible to reduce the data to a motional correlation time. It is a property of polyTMG to crystallize near room temperature, and indeed the very short T_{CH} values indicate crystalline material in these samples. The decay curves (Figure 5) for determining $T_{1\rho}{}^{H}$ are not obviously biphasic, leading to the conclusion that the components either are not relaxation resolved or are averaged. The general trend in the data can be explained from the semicrystalline nature of the system with the assumption of spin diffusion among protons of the separate domains[18] yielding an average value of $T_{1\rho}{}^{H}$. Presumably if one had $T_{1\rho}{}^{H}$ values for pure amorphous and pure crystalline polyTMG, one could calculate via a simple weighted linear additivity of relaxation rates[18,19] the relative content of each at a given extension. Applying this idea to the data in Table I for the nonspinning samples for the $\lambda = 4.5$ sample and assuming that the $T_{1\rho}{}^{H}$ values for $\lambda = 1$ and 6.2, respectively, are for a pure amorphous and pure crystalline CH_2 segment, one calculates about a 30% amorphous phase. This agreement with the amount of bulk mobility component for the $\lambda = 5$ sample determined from T_{CH} and from T_2* suggests that there is extensive spin diffusion averaging the observed values. Thus the variation in $T_{1\rho}{}^{H}$ at least in part appears to arise from averaging over domains of crystalline and amorphous segments. Because of the short values of $T_{1\rho}{}^{H}$, these domains must be quite small, on the order of 30 Å.[18,19] While these agreements on the fraction of the amorphous phase are reassuring, the fact that the CH_2 and OCH_2 protons do not have anywhere near the some relaxation times argues against spin diffusion as being dominant. We have no explanation for this observation. This dependence of $T_{1\rho}{}^{H}$ on extension was not observed for the polyester–polyurethane Lycra 128,[10] which is not significantly crystalline at moderate extensions.

Since $T_1{}^{H}$ is longer than $T_{1\rho}{}^{H}$ (Table II), it is subject to more extensive spin diffusion averaging of domains and should change markedly as the extension increases the relative amount of crystallinity. Interestingly, $T_1{}^{H}$ increases with extension, indicating that more crystalline segments with their expected longer relaxation times are contributing to the averaged value observed. In this case the CH_2 and OCH_2 resonances have virtually the same $T_1{}^{H}$ and $T_1{}^{C}$ in the unstretched samples.

Table II
Proton and Carbon Relaxation Parameters for Lycra 146 at Extensions of 1 and 5

	segment extension	CH_2: 26.4 ppm	OCH_2: 70.5 ppm
$T_1{}^{H}$, s	1	0.23	0.22
	5	0.45	0.44
$T_1{}^{C}$	1	0.07	0.09
via CP	5	0.19, 36	0.19, 23 (70 ppm)
			0.28, 58 (72 ppm)
T_2*, ms	1	1.2	1.2
via CP	5	0.02 (62%)[a]	0.02 (70%)[a]
		0.8 (38%)[a]	0.8 (30%)[a]
T_2*, ms	1	1.2	1.2
via DP		15	14
300-s delay			
	5	0.02 (62%)[a]	0.02 (73%)[a]
		0.9 (38%)[a]	0.9 (27%)[a]
T_2*, ms	5	0.03 (50%)[a]	0.03 (62%)[a]
1-s decay		1.0 (50%)[a]	1.0 (38%)[a]

[a] Percent of carbons in the domain with this T_2*.

$T_1{}^{C}$ behaves somewhat similarly to $T_1{}^{H}$ in increasing with extension; however, it is clearly less subject to spin diffusion averaging. In the extended sample two distinct relaxation times result from fitting the decay to two components (Table II), the time for the polyTMG crystalline domain being dramatically longer than that for the amorphous domain. These $T_1{}^{C}$ data were acquired through CP spin preparation and thus may be skewed to favor the observation of rigid domains.

Reliable quantitation of the amounts of each domain can only be made if the spins of each domain are observed with equal sensitivity. We have followed the ^{13}C intensity as a function of delay after the spin preparation in modification of the dipolar dephasing technique of Alla and Lippmaa[20] to measure T_2* exponential decay for species of widely different time constants. Table II lists sets of T_2* determined for several spin preparation methods. The unstretched samples give a major component with the same T_2* of 1.2 ms for both CP and DP pulse sequences. There is also a very long T_2* component in the unstretched sample. This long component undoubtedly arises from the amorphous or bulk mobility polyTMG segments. The 1.2-ms component seen by both CP and DP is a less mobile component which we attribute to segments sufficiently restrained to be cross polarized but is neither crystalline nor freely mobile. For the stretched sample, this component has a shorter T_2* of 0.8 ms and is only 30% of the signal; the dominant component has a very short T_2* of 0.02 ms. The results for CP and DP for the stretched sample agree well within experimental error both for the values of T_2* and for the quantitative contribution. This agreement indicates that there is very little amorphous segment mobility in the stretched sample. Furthermore, these CP and Bloch decay domain compositions are in agreement with the analysis of multiple T_{CH} contributions to the cross-polarization dynamics (Table I), giving further assurances that quantitative estimates are reasonable. Reduction of the recycle time of the DP sequence will not allow the crystalline domain spins of long $T_1{}^{C}$ to fully equilibrate and thus they are reduced in relative intensity. This distortion of relative intensities is illustrated in the T_2* data in Table II for DP with a 1-s recycle delay.

The use of these relaxation times is subject to the uncertainty that spin diffusion of magnetization between domains would give an erroneous amount estimated for each domain. CRAMPS experiments would measure such effects, but these techniques are not available in our laboratory. However, as the T_{CH} values are somewhat longer than T_2^* for the same sample, one would expect the former to give different relative amounts of domains if interdomain spin diffusion were important. Since the soft segment quantitation from T_2^* agrees rather satisfactorily with the values from T_{CH}, this argues that spin diffusion between domains is not important.

The above data show that MAS-NMR observations can yield information about all regions of a multiphase system such as the polyether–polyurethane TPE especially through comparison of the relaxed and stretched specimens. The relatively simple NMR techniques and the well-developed theory make it a valuable additional technique to complement the commonly used crystallinity selective techniques of X-ray and DSC.[4,5] A recent CPMAS study of unstretched polyurethanes focuses on the hard segment crystallinity[21] in a way complementary to this study.

Acknowledgment. We are grateful to E. I. du Pont de Nemours and Co. for the gift of research samples of Lycras through Dr. John Boliek.

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